XXIII. *Experiments on the Tranſmiſſion of the Vapour of Acids through an hot earthen Tube, and further Obſervations relating to Phlogiſton.* *By the Rev.* Joſeph Prieſtley, *LL.D. F. R. S.*

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IN my late experiments on the *phlogiſtication of ſpirit of nitre by heat* it appeared, that when pure air was expelled from what is called dephlogiſticated ſpirit of nitre, the remainder was left phlogiſticated. This I find abundantly confirmed by repeating the experiments in a different manner, and on a larger ſcale; and I have applied the ſame proceſs to other acids and liquors of a different kind. From theſe it will appear, that oil of vitriol and ſpirit of nitre, in their moſt dephlogiſticated ſtate, conſiſt of a proper ſaturation of the acids with phlogiſton, ſo that what we have called the *phlogiſtication* of them, ought rather to have been called their *ſuper-phlogiſtication.*

I began with treating a quantity of oil of vitriol as I had done the ſpirit of nitre, *viz.* expoſing it to heat in a glaſs tube, hermetically ſealed, and nearly exhauſted; and the reſult was ſimilar to that of the experiment with the nitrous acid, with reſpect to the expulſion of air from it, though the phlogiſtication not appearing by any change of *colour*, I did not in this method aſcertain that circumſtance. The particulars were as follows.

After the acid had been made to boil ſome time, a denſe white vapour appeared in quick motion at a diſtance above the acid,

acid, and though, on withdrawing the fire, that vapour diſappeared, it inſtantly re-appeared on renewing the heat. When the tube was cool, I opened it under water, and a quantity of air ruſhed out, though the acid had been made to boil violently while it was cloſing, ſo that there could not have been much air in the tube. This air, which muſt therefore have been generated in the tube, was a little worſe than common air, being of the ſtandard of 1.12 when the latter was 1.04. I repeated the experiment ſeveral times, and always with the ſame reſult.

That this air ſhould be worſe than common air, I cannot well explain. But in my former experiments it appeared that vitriolic acid air injures common air; and that in proportion as pure air is expelled from this acid, the remainder becomes phlogiſticated, or charged with vitriolic acid air, clearly appeared in the following experiment.

Making a quantity of oil of vitriol boil in a glaſs retort, and making the vapour paſs through a red-hot earthen tube, glazed inſide and out, and filled with pieces of broken tubes, I collected the liquor that diſtilled over, and found it to be the ſame thing with water impregnated with vitriolic acid air. The ſmell of it was exceedingly pungent, and it was evident, that more of this air had eſcaped than could be retained by that quantity of water. The oil of vitriol uſed in this proceſs was 1 oz. 9 dw. 18 gr. and the liquor collected was 6 dw. 12 gr. When I collected the air that was produced in this manner, which I did not do at this time, it appeared to be very pure, about the ſtandard of 0.3 with two equal meaſures of nitrous air.

At another time, expending 1 oz. 11 dw. 18 gr. of oil of vitriol, of the ſpecific gravity of 1856 (that of water being 1000),

1000), I collected 19 dw. 6 gr. of the volatile acid, of the ſpecific gravity of 1340, and 130 oz. meaſures of dephlogiſticated air of the pureſt kind, *viz.* of the ſtandard of 0.15.

It is eaſy in this manner to collect a great quantity of dephlogiſticated air; but the principal objection to the proceſs is, that after uſing a few times, the earthen tubes become tender, and too eaſily break, eſpecially in heating or cooling. It is alſo difficult to lute the retort containing the acid and the earthen tube. The air produced in this manner is filled with the denſeſt white cloud imaginable.

Going through the ſame proceſs with ſpirit of nitre, the reſult was in all reſpects ſimilar, but much more ſtriking, the production of both dephlogiſticated air and phlogiſticated acid vapour being prodigiouſly quicker, and more abundant. Expending 5 oz. 8 dw. 6 gr. of ſpirit of nitre, I collected 600 oz. meaſures of very pure dephlogiſticated air, being of the ſtandard of 0.2. I alſo collected 1 oz. 7 dw. 14 gr. of a greeniſh acid of nitre, which emitted copious red fumes. All the apparatus beyond the hot tube was filled with the denſeſt red vapour, and the water of the trough in which the air was received was ſo much impregnated with it, that the ſmell was very ſtrong; and it ſpontaneouſly yielded nitrous air ſeveral days, juſt as water does when impregnated with nitrous vapour. Perceiving the emiſſion of air from the water, after it had ſtood ſome time, I filled a jar containing 30 oz. meaſures with it, and without any heat it yielded two oz. meaſures of the ſtrongeſt nitrous air.

Taking the ſpecific gravity of the acid before and after this diſtillation, the former was to the latter as 1471 to 1182. When the weight of the air produced in this experiment, and that of the liquor diſtilled, is compared with that of the acid

before diſtillation, it will appear, that there muſt have been a great loſs of acid vapour, which was either retained in the water of the trough, or eſcaped through it.

I do not ſee that theſe experiments can be explained, but on the ſuppoſition that the moſt dephlogiſticated oil of vitriol and ſpirit of nitre are, in a proper ſenſe, ſaturated with phlogiſton; and that when part of the acidifying principle is expelled in the form of the air, the remainder is ſuperſaturated with it.

To try whether the acid, thus ſuperſaturated with phlogiſton, was convertible into pure air by this proceſs, I heated the liquor collected after the diſtillation of the oil of vitriol, that is, water impregnated with vitriolic acid air, and made the vapour paſs through the hot tube, but no air came from it; and when collected a ſecond time, it was not at all different from what it had been before. The ſpecific gravity was alſo the ſame.

It is evident, however, though this proceſs does not ſhew it, that the volatile vitriolic acid contains the proper element of dephlogiſticated air; ſince by melting iron in vitriolic acid air, a quantity of fixed air (which is compoſed of inflammable and dephlogiſticated air) is produced. Melting iron in 9 oz. meaſures of vitriolic acid air, it was reduced to 0.3 oz. meaſures, and of this 0.17 oz. meaſures was fixed air. I repeated the experiment with the ſame reſult, and putting the reſiduums together found the air to be inflammable.

But the reſult was ſomething different when I ſent through the hot tube the liquor that I had collected in the proceſs with ſpirit of nitre. No air, however, was produced at the firſt, nothing appearing beſides a *red vapour* that was wholely abſorbed by water, or eſcaped through it into the atmoſphere; but towards the end of the proceſs I collected 10 oz. meaſures of dephlo-

dephlogiſticated air. The quantity of the liquor expended was about 2 oz. meaſures. It may, however, be preſumed, that this ſmall quantity of air came from ſome of the acid which eſcaped the action of the fire in the former proceſs. Indeed its coming at the laſt only may be conſidered as a proof of this, as all the more volatile acid, which came over firſt, yielded no air.

I ſubmitted a quantity of *ſpirit of ſalt* to both theſe proceſſes, *viz.* expoſing it to a boiling heat in glaſs tubes, hermetically ſealed, and making the vapour paſs through a red hot earthen tube, but no air was produced in either caſe. In the former caſe, the water ruſhed into, and completely filled, the tube, when it was opened under water; and in the other proceſs the liquor diſtilled was preciſely of the ſame ſpecific gravity, and, no doubt, in all other reſpects, the ſame as before diſtillation; but the acid that remained in the retort was of leſs ſpecific gravity, in conſequence of the acid vapour being expelled by the heat in the form of marine acid air, which appeared not to be affected by a red heat.

Though, in the proceſs with ſpirit of ſalt, the reſult be different from that of thoſe with oil of vitriol and ſpirit of nitre, yet there is an analogy among all theſe three acids in this reſpect, *viz.* that the marine and both the volatile acids of vitriol and nitre are made by impregnating water with the acid vapour, ſo that in its uſual ſtate it may be ſaid to be phlogiſticated as well as theſe.

It was evident that the water in the worm-tub was much more heated by the diſtillation of the ſpirit of ſalt than by that of the oil of vitriol, and eſpecially that of the ſpirit of nitre; ſo that much of the heat by which it had been raiſed in vapour muſt, in the latter caſe, have been *latent* in the air that was

formed; whereas, in the other caſe, it was communicated to the water in the worm-tub.

In one of the proceſſes with boiling ſpirit of ſalt, in a glaſs tube, hermetically ſealed, I had the ſame white vapour dancing in the middle of the tube as in the experiment with the oil of vitriol; but this tube burſt, and I never had the ſame appearance again, though I repeated the experiment ſeveral times for the ſake of it.

The vapour of dephlogiſticated marine acid, which M. BERTHOLLET diſcovered, and with which water may be impregnated as with fixed air, being made to paſs through the hot earthen tube, became dephlogiſticated air as in the following experiment.

Having poured a quantity of ſpirit of ſalt upon ſome manganeſe in a glaſs retort, I heated it as in the preceding experiments with a proper apparatus both for receiving the diſtilled liquor, and the air. I found ſeven-tenths of the air was fixed air, and the remainder very pure dephlogiſticated. The quantity I could not meaſure on account of one of the junctures in the apparatus giving way; but I do not imagine that quite ſo much pure air could be got in this method as from the manganeſe itſelf in a direct proceſs. The liquor received in this diſtillation reſembled ſtrong ſpirit of ſalt in which manganeſe had been put.

This proceſs immediately ſucceeding that in which the glaſs tube, joining the earthen tube and worm-tub, was left full of black matter by the diſtillation of the alkaline liquor (which will be mentioned hereafter), the blackneſs preſently vaniſhed, and the tube became tranſparent as before. On this account, however, it is poſſible that I might receive leſs pure air than I ſhould otherwiſe have done.

Diſtilled

Diſtilled vinegar ſubmitted to this proceſs yielded air two-thirds of which was fixed air, and the reſt inflammable: expending 2 oz. 19 dw. 0 gr. of the acid, I got 1 oz. 19 dw. 0 gr. of a liquor which had a more pungent ſmell than it had before diſtillation. It had alſo ſome black matter in it, and ſome of the ſame remained at the bottom of the retort when the liquor was evaporated to dryneſs. The air I received was 90 oz. meaſures.

Alkaline air is converted into inflammable air in this proceſs as well as by the electric ſpark, but by no means, I think, in ſo great a degree. I put 2 oz. 10 dw. 0 gr. of water pretty ſtrongly impregnated with alkaline air into the retort, and heating it, ſent the vapour through the hot tube; when I collected 2 oz. 3 dw. 0 gr. of liquor, which had a diſagreeable empyreumatic ſmell, as well as that of a volatile alkali, and it was quite opaque with a *black matter*, which ſubſided to the bottom of the veſſel. Alſo the tube through which the air and vapour had been conveyed was left quite black, as mentioned above. One of the junctures of the apparatus not having been air-tight, I did not collect all the air, but it came only at the beginning of the proceſs, and before the tube became black, or any liquor was diſtilled, and it was all ſtrongly inflammable.

I ſhall now recite a few experiments of a different kind from thoſe that have been mentioned above, and more immediately relating to the doctrine of phlogiſton.

It is ſaid, by thoſe who do not admit the doctrine of phlogiſton, that the metals are ſimple ſubſtances, which, having a ſtrong affinity to dephlogiſticated air, imbibe it when they become calces, without parting with any thing. But that ſomething is really parted with in the calcination (as they will call

it) of iron in dephlogiſticated air, appears to me to be very evident, as well as in the proceſs with ſteam.

That fixed air is found in the veſſel in which iron is melted in dephlogiſticated air, I obſerved before; but I never took much care to aſcertain the quantity of it. This I have lately done in many inſtances, and in all of them find it to be much more conſiderable than can be accounted for, by ſuppoſing it to come from plumbago in the very ſmall quantity of iron that I melted; ſo that it muſt neceſſarily have been formed by the phlogiſton from the iron, and the pure air in the veſſel, at the ſame time that the iron became finery cinder by imbibing water from the air; and I have ſhewn, that by far the greateſt part of the weight of this air is water. The experiments were made with a very good burning lens, of ſixteen inches diameter, with which Mr. PARKER has generouſly furniſhed me; and by means of it I can now make theſe experiments, which require a great degree of heat, with much more eaſe and certainty than I could do before.

In $6\frac{1}{2}$ oz. meaſures of dephlogiſticated air I melted turnings of malleable iron till there remained only $1\frac{1}{3}$ oz. meaſure, and of this $\frac{2}{3}\frac{7}{0}$ oz. meaſure was fixed air. In 6 oz. meaſures of dephlogiſticated air, of the ſtandard of 0.2, I melted iron till it was reduced to two-thirds of an ounce-meaſure, of which one-half was fixed air, and the remainder completely phlogiſticated. Again, I melted iron in $7\frac{1}{2}$ oz. meaſures of dephlogiſticated air, of the ſame purity with that in the laſt experiment, when it was reduced to $1\frac{1}{3}$ oz. meaſure, and of this four-fifths was fixed air, and the remainder phlogiſticated. In this caſe I carefully weighed the finery cinder that was formed in the proceſs, and found it to be nine grains, ſo that the iron that had been melted (being about two-thirds of this weight) had

had been about ſix grains. I repeated the experiment with the ſame reſult.

When the dephlogiſticated air is more impure, the quantity of fixed air will always be leſs in proportion. Thus, having melted iron in ſeven ounce meaſures of dephlogiſticated air of the ſtandard of 0.65, it was reduced to 1.6 oz. m.; and of this only one-third of an ounce meaſure was fixed air. This, however, is much more than can come from the plumbago in the iron; but as the production of this fixed air is by many aſcribed to this plumbago, it may be worth while to ſhew by computation that it is impoſſible that it ſhould have this origin. Both the quantity of plumbago in iron, and the quantity of fixed air in plumbago, are much too ſmall for the purpoſe.

From half an ounce of the pureſt plumbago, I firſt got, in a coated glaſs retort, 13 ounce-meaſures of air, of which only three ounce meaſures were fixed air, the reſt being inflammable; then putting it into an earthen tube, I kept it ſome hours in as great a heat as I could produce, and got 22 oz. m. more; and of this alſo only three were fixed, and the reſt inflammable, and the laſt portion was wholly ſo.

But inſtead of ſuppoſing the fixed air that I got to be that which was expelled from the plumbago in the iron, I will ſuppoſe that even the whole of this plumbago afforded only one of the elements of the fixed air, *viz.* phlogiſton, or that which the French chemiſts call *carbone*; and that this principle, by its union with the dephlogiſticated air in the veſſel, forms the fixed air, yet on this moſt unfavourable and improbable ſuppoſition the quantity will be found to be inſufficient.

If 100 gr. of iron contain, according to M. BERGMAN, 0.12 gr. of plumbago, 7 gr. (which is the moſt that in any of the preceding proceſſes I converted into finery cinder) would

contain only 0.0084 gr. of plumbago; and if we ſuppoſe with Mr. KIRWAN, that an hundred cubic inches of fixed air contains 8.14 gr. of phlogiſton, the fixed air produced in one of the above-mentioned proceſſes (*viz.* four-fifths of an ounce-meaſure) would contain .032 gr. of phlogiſton, which is above three times more than the plumbago in the iron could furniſh. It is evident, therefore, that the quantity of fixed air that I found muſt have been formed by phlogiſton from the iron uniting with the dephlogiſticated air in the veſſel.

If, as I have inferred, from burning charcoal of copper in dephlogiſticated air (ſee Experiment, Vol. VI. p. 272.) fixed air conſiſts of 3.45 parts of dephlogiſticated air and 1.5 of phlogiſton, it will be found, that four-fifths of an ounce meaſure of fixed air will contain 0.21 gr. of phlogiſton, which is much more than on the ſuppoſition of Mr. KIRWAN.

Another argument againſt the antiphlogiſtic doctrine may be drawn from an experiment which I made upon Pruſſian blue; if the ſmall quantity of fixed air, that may be expelled from it by heat, be compared with the much greater quantity which is produced when heated in dephlogiſticated air.

Pruſſian blue is generally ſaid to be a calx of iron ſuperſaturated with phlogiſton, though of late it has been ſaid by ſome that it has acquired ſomething that is of the nature of an *acid*. From my experiments upon it, with a burning lens in dephlogiſticated air, I ſhould infer, that the former hypotheſis is true, except that the ſubſtance contains ſome fixed air, which is no doubt an acid; for much of the dephlogiſticated air diſappears, juſt as in the preceding ſimilar proceſs with iron.

I threw the focus of the burning lens upon 2 dw. 5 gr. of Pruſſian blue in a veſſel of dephlogiſticated air, of the ſtandard of 0.53, till all the colour was diſcharged. Being then weighed,

weighed, it was 1 dw. 2 gr. In this proceſs 7¼ oz. of fixed air had been produced, and what remained of the air was of the ſtandard of 0.94. Heating the brown powder to which the Pruſſian blue was reduced in this experiment in inflammable air, it imbibed 8½ oz. m. of it, and became of a black colour; but it was neither attracted by the maguet, nor was it ſoluble in oil of vitriol and water, as I had expected it would have been.

Again, I heated Pruſſian blue in dephlogiſticated air, of the ſtandard of 0.2, without producing any ſenſible increaſe of its bulk, when I found three ounce meaſures of it to be fixed air, and the ſtandard of the reſiduum, with two meaſures of nitrous air, was 1.35. The ſubſtance had loſt eleven grains, the greateſt part of which was evidently water.

To determine what quantity of fixed air Pruſſian blue would yield by mere heat, I put half an ounce of it into an earthen tube, and got from it 56 oz. m. of air, of which 16 oz. m. were fixed air, in the proportion of one-third in the firſt portion, and one-fourth in the laſt. The remainder was inflammable. There remained 5 dw. 20 gr. of a black powder, with a very little of it (probably the ſurface) brown.

Comparing theſe experiments, it will appear, that the fixed air procured by means of Pruſſian blue and dephlogiſticated air muſt have been formed by phlogiſton from the Pruſſian blue and the dephlogiſticated air in the veſſel: for if 240 gr. of this ſubſtance yield 16 oz. meaſures of fixed air, ten grains of it (which is more than was uſed in the experiment) would have yielded only 0.6 oz. m. Nor is it poſſible to account for the diſappearing of ſo much dephlogiſticated air, but upon the ſuppoſition of its being employed in forming this fixed air.